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A study of Toray's negative working driographic printing plate and the effect ink tack has on toning in the non-image area

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Certificate of Approval -- Master's Thesis

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CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's Thesis of

LARRY MICHAEL CAPITANO

With a major in Printing Technology
has been approved by the Thesis Committee as satisfactory for the thesis requirement for the Master of Science degree at the convocation of

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date

Thesis Committee:

Thesis Advisor

Graduate Program Coordinator

Director of the School of Printing

ACKNOWLEDGEMENT

During the course of time it took to complete this thesis writing an acknowledgement was never a great concern. Now it is time to give thanks, where does one begin and end? It is said that any one event or individual can alter a persons life. To mention a few which had an impact on my life and to acknowledge the gratitude they so justly deserve a short, and far from complete, list has been compiled.

Frank Cost - graduate coordinator and friend.
My Parents - for life and loving patience.
DMA - for the opportunity to continue my education.
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Ruth Terry - an incredible lady.
Pittman - for the supplies required for testing.

Thanks to each of you for the help and the memories you have given me, I will never forget.

LARRY CAPITANO

A STUDY OF TORAY'S NEGATIVE WORKING DRIOGRAPHIC PRINTING PLATE AND THE EFFECT INK TACK HAS ON TONING IN THE NON-IMAGE AREA

by
Larry M. Capitano

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ABSTRACT

Driography is a planographic printing process. A driographic printing plate differs from a conventional offset lithographic plate in that water is not required to keep the non-image area clean of ink during printing. Water, or fountain solution, is not required during printing because a silicone rubber coating which repels ink is used for the non-image area of a driographic plate. The first driographic plate was introduced in the early 1970's by the 3M Company. The plate was a positive working printing plate and has since been discontinued. Driography has since been researched by a number of companies but only one is presently marketing a driographic plate. The Toray Company, a Japanese based firm, is producing a negative working driographic printing plate.

The purpose of this study is to research Toray's negative working driographic printing plate. It is hypothesized that as ink tack decreases, toning in the non-image area will increase. In this experiment, ink tack was monitored at the point of impression using a thermocouple device. The thermocouple was used to measure ink temperature on an inking form roller. Temperature/tack curves were developed and used to convert ink temperatures to tack readings. The actual experiment was performed on a duplicator offset printing press. A second technique using ink tack-reducer to alter ink tack was performed as an alternative test to support the initial method results.

During the course of the study a number of variables could have altered the test results. These variables were monitored and kept constant during testing. The variable which affected test results most dramatically was the oil content in the ink. It was concluded that the amount of oil content in an ink had more influence on the degree of toning than ink tack did as originally hypothesized.

CHAPTER 1

INTRODUCTION

BRIEF HISTORY OF DRIOGRAPHY

Alois Senefelder invented lithography in 1798 using a greasy ink and a slab of porous limestone.[1] The lithographic process has progressed since its invention but the basic principle, grease and water do not readily mix, remains.

Conventional lithography requires fountain solution to prevent the non-image area of the plate from printing. Driography is a form of lithography which eliminates the need for fountain solutions. The non-image area of the plate is coated with a silicone compound which repels ink. The first driographic plate introduced in the United States was in 1971 by the 3M Company.[2] Since 1971, Itek, Kodak, and Scott have been granted patents which involve driography.[3] In 1980, Toray, a Japanese Firm, introduced their driographic plate.[4]

PRINCIPLE ASPECT OF DRIOGRAPHY

As a form of lithography, driography has many of the advantages and some of the disadvantages of lithography. Driography also has advantages and disadvantages lithography does not. Most advantages of driography can be attributed to the elimination of the need for fountain solutions.

ADVANTAGES OF DRIOGRAPHY

1. Constant monitoring and readjusting of ink/water balance during printing no longer has to be maintained resulting in more consistent color throughout press-run.
2. Paper waste during press make-ready is reduced considerably (as much as 80%).
3. Elimination of paper curl because of moisture problems caused by fountain solution.[5]
4. Registration capabilities are not hindered by dimensional stability of paper because of moisture pick-up during press operation.[6]
5. Removal of water fountain dampening systems would lower press cost and engineering complexity.[7]
6. Shorter exposure times increase production rate and extends life of light source.
7. Excellent dot reproduction is achieved, 2-5% highlight and 95% shadow. This is apparently possible because of the grainless plate surface.
8. Reduced dot gain on press, approximately 6-7% in midtones compared to a normal 15% using conventional plates. This allows heavier ink film thicknesses without plugging problems.
9. Poor contact during exposure process can often be corrected for by monitoring development time; conventional plates would normally be disposed of.

10. Potential markets include high quality sheet fed and color web fed printing with run lengths up to 200,000 impressions.

11. Appealing to speciality printers, especially on non-absorbent stocks such as plastics, PVC, heat transfer papers, gummed stocks, and metal decorating.[8]

12. Elimination of fountain solution expense and the cost of air circulation apparatus.

13. Avoids Environmental Protection Agency and OSHA problems caused by alcohol in fountain solution.[9]

DISADVANTAGES OF DRIOGRAPHY

1. Press and ambient temperature must not rise to a point which causes ink vehicle break down leading to non-image area accepting ink (toning). Press temperature can be minimized by reducing roller pressure therefore reducing friction which causes temperature to decrease.

2. High ink tack requirements may cause paper picking problems with lower grade stock, especially in large solid areas.

3. No water to act as a conductive pathway for static charge could cause paper handling problems, especially if pressroom has low humidity.

4. Development time may be as much as 50% longer than a conventional plate, depending on the type of driographic plate used.
5. Inferior paper or board causes abrasion problems of non-image area over long runs because lint builds up between plate and blanket.[10]

DRIOGRAPHIC PLATE SURFACE CHARACTERISTICS

Driography is a lithographic printing process. Lithography differs from other major printing processes by using a planographic printing surface. The image and non-image areas are essentially on a flat surface and are kept separate during the printing process chemically.[11] The difference between driography and conventional offset lithography is the requirements for printing. Offset lithography is based on the principle that grease and water do not readily mix. It requires fountain solution to maintain the non-image area from printing. Driography eliminates the requirement of fountain solution by using a rubber silicone compound that repels ink from the non-image area of the plate.

IMAGE AREA OF A DRIOGRAPHIC PLATE

The image material on a conventional lithographic plate is oleophilic (oil loving) and hydrophobic (water hating).[12] The image material for a driographic plate must also be oleophilic but not necessarily hydrophobic. The image material for either plate must adhere well to the plate surface, resist abrasion, be light sensitive, and chemically resistant. The image material used for Toray's negative working plate is a diazo compound similar to the image material used on a conventional lithographic plate.[13]

NON-IMAGE AREA OF A DRIOGRAPHIC PLATE

A driographic plate's non-image area must repel ink without assist from fountain solution or gum arabic. The silicone rubber compound which is used is a smooth substance which has a low surface energy (a low cohesion between molecules).[14] When driographic plates were first marketed by 3M, the silicone rubber exhibited poor abrasion resistance. Toray reformulated the silicone rubber compound to increase surface abrasion resistance.[15] Toray's patent does not describe how the abrasion resistance was increased but it does mention the attribute. For additional protection a protective sheet is used to secure against mishandling.

TORAY PLATE MAKE-UP

Toray Industries manufactures several types of driographic plates. Initially, they produced a positive working driographic plate. In 1978, Toray obtained a patent from the United States Patent Office (patent number 4,086,093) for a dry planographic printing plate. It is a negative working driographic plate described in the patent as follows:

1. The base material could be a coated paper, metal, or a plastic such as polyethylene terephtable. The base material should be sufficiently flexible for mounting on a lithographic press, strong enough to withstand the load normally produced by a lithographic press, and be dimensionally stable to ensure proper registration throughout press run. The base layer is impregnated with or dispersed within an ultraviolet light absorbing agent.
2. An anti-halation layer, which should have good adhesion qualities, is coated onto the base. It is noted here that this coating is normally coated beneath a photosensitive resin layer in the production of ordinary lithographic printing plates but, because of the structure of driography, this is not done.
3. A thin silicone primer is coated onto the halation -preventing coat and acts as a surface treating agent for better adhesion of next layer.

4. A silicone rubber layer is coated onto the base material. To increase abrasion resistance, a filler is mixed with the silicone rubber before coating. A small amount of photo sensitizer is mixed with the silicone rubber which enhances the adhesion of the next layer.

5. A photo adhesive layer overlies the silicone rubber layer, comprising at least one photopolyerizable unsaturated compound having a boiling point about 100^{o}C and a photoinitiator.

6. A thin transparent protective film or a polymer solution is incorporated to protect plate coating from mechanical damage and inhibit osmosis into the photoadhesive layer promoting photopolymerization. The film is removed by peeling or dissolution in the developing step.[16]

TORAY PLATE EXPOSURE

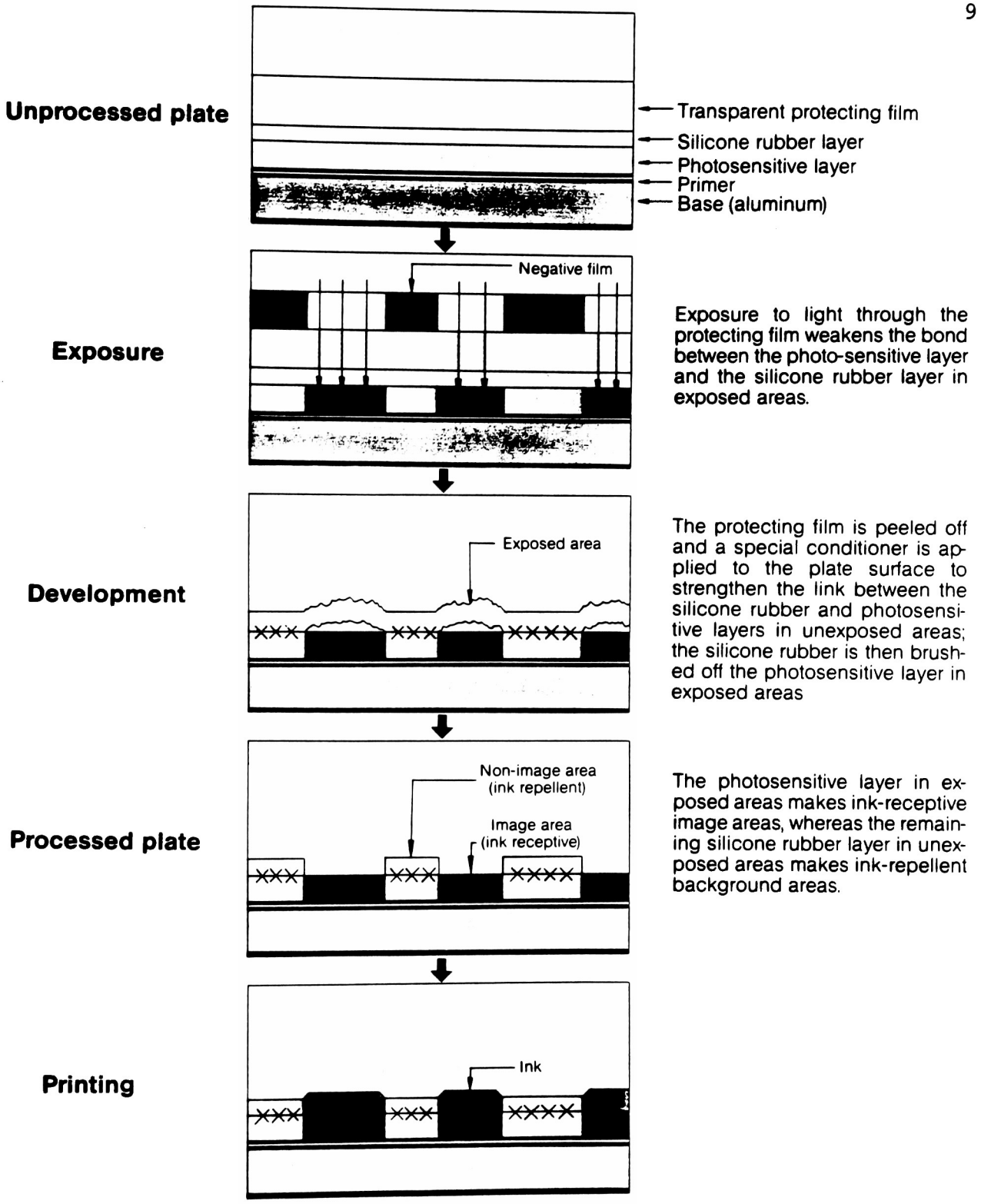
A conventional lithographic plate exposure unit is used to expose Toray negative working driographic printing plates. A film negative is placed on the plate, put under vacuum, and the actinic light exposes the plate. The plate sensitivity is in the ultraviolet and blue range of the spectrum.

Upon exposure to light, the photoadhesive layer hardens by a photopolyerization cross-linking reaction. Exposure causes the photoadhesive layer to adhere strongly to the underlying silicone rubber layer. If a peel type protective

layer is used then when the protective layer is peeled off the unexposed photoadhesive layer will be removed. In this application, the developing operation is completed. If a protective layer was coated on then the unexposed layer is removed with a developing liquid. The later is the type used in this experiment.

In some applications, it is possible to expose or heat the entire plate surface to increase adhesion between the photoadhesive layer and the silicone rubber layer. It is an extra step which would be necessary only to increase run length on press.

Minor scratches or other unwanted spots can be removed by applying a silicone liquid solution with a special applicator. Additions to image areas are made with a stencil pen by scratching the silicone rubber layer. These operations can be done while plate is on press similar to conventional deletion and addition operations.



Structure and Working Principle of a Toray Negative Acting Driographic Plate.

FIGURE 1

FOOTNOTES FOR CHAPTER 1

[1]Charles Shapiro, The Lithographer's Manual, Fifth Edition (The Graphic Arts Technical Foundation, Inc., 1974), p.1:1.

[2]"Where Are We With Waterless Printing?", Drucker Papers, 121, No. 6 (March 21, 1983), pp. 3-4.

[3]S.L. Gaudioso, "Mechanisms of Ink Release in Waterless Lithography", TAGA Conference Proceedings (1975), pp.177-194.

[4]"Where Are We With Waterless Printing?"

[5]S.L. Gaudioso, pp. 177-194.

[6]T.J. Pacansky, "Materials Criteria for Waterless Lithography", TAGA Conference Proceedings (1975), pp. 195-219.

[7]Gaudioso, pp. 177-194.

[8]"Waterless Offset Lithography - Has It Arrived?" Ink and Print, 1, No. 3, (Winter '83), pp. 27-30.

[9]Gaudioso, pp. 177-194.

[10]"Waterless Offset Lithography - Has It Arrived?", pp. 27-30.

[11]Paul J. Hartsuch, Ph.D., Chemistry for the Graphic Arts, (Graphic Arts Technical Foundation, 1979), p. 140.

[12]Ibid

[13]U.S. Patent, Dry Planographic Printing Plate, No. 4,086,093, April 25, 1978.

[14]S.L. Gaudioso, pp.177-194.

[15]"Waterless Offset Lithography - Has It Arrived?", pp. 27-30.

[16]U.S. Patent No. 4,086,093.

CHAPTER 2

STATEMENT OF PROBLEM

In the early 1970's, the first driographic printing plate was produced by the 3M Company.[1] Since its introduction, driography has been researched by a number of corporations including Xerox and Scott.[2] Research reports and feedback from actual production shops which use driographic plates determined the main disadvantage they found with driography was the need for high tack inks to avoid scumming in the non-image area.[3] Production workers do not have the equipment or desire to research the reason high tack inks are required. A printer is more concerned with the solution to keep the ink from scumming so production can be maximized. Researchers in the graphic arts are concerned with why and therefore what can be done to solve the problem. For one to understand why high tack inks are required, the basis of lithography must be understood.

The phenomena of lithography, the transfer of ink from a planographic surface, occurs for several reasons. The non-image material when properly treated will retain water. This is accomplished by coating the plate with gum arabic which allows the non-image area to retain the fountain solution. The fountain solution is mechanically held to the plate by the plate grain and chemically held by the gum arabic. When ink is transferred to the plate the wet

non-image area will repel the ink. If any ink does transfer to the non-image area it will mix with the fountain solution. The fountain solution will dilute the ink lowering the tack. As the plate cylinder rotates the ink form rollers, which are coated with a higher tack ink, will pick up the ink from the non-image area (back-trap) and redistribute it into the ink train.

Keeping the preceding phenomena in mind and using a model developed by Xerox the principle of driography, waterless printing, can be explained. The non-image area of the plate is extremely oil resistant and has a low surface energy (a low cohesion between molecules) which essentially repels most materials. Even under these conditions the material (silicone rubber) still tends to pick up ink if conditions are not correct. The ink must have a high tack and a high surface energy. In this state, the ink will diffuse a slight layer of solvent onto its surface. This layer is what splits between the ink form rollers and non-image area of the plate avoiding an undesired ink transfer. In this model, it is not the surface energy of the materials involved (silicone rubber and ink) which is of importance. It is the ability of the ink to diffuse a solvent of lower viscosity than the ink itself onto the outer layer. If this solvent is not present, the result is toning, a problem which, when solved, will make

the application of driography more appealing to printers. This model is what the Xerox Corporation referred to as "The Weak Fluid Boundary Layer Model" and was formulated while doing research on 3M's driographic printing plate.[4]

FOOTNOTES FOR CHAPTER 2

[1]"Where Are We With Waterless Printing?", Drucker Papers, 121, No.6 (March 21, 1983), pp.3-4.

[2]S.L. Gaudioso, "Mechanism of Ink Release in Waterless Lithography", TAGA Conference Proceedings (1975), pp. 177-194.

[3]"Waterless Offset Lithography - Has It Arrived?", Ink and Print, 1, No. 3, (Winter '83), pp. 27-30.

[4]S.L. Gaudioso, pp. 177-194.

CHAPTER 3

RELATED LITERATURE

Since 3M introduced their driographic plate, other companies have filed patents for similar driographic plates and processes. Xerox is a company which took particular interest in researching the mechanisms of ink release principles in driography. The 1975 TAGA (Technical Association in the Graphic Arts) Proceedings included a research report by Xerox which formulated several models about driographic ink release.

Surface Energy Model. Surface energy is the cohesion between molecules within a substance or material. In this model the criteria of ink release is that the cohesion of molecules within the ink must be greater than the adhesion between the ink and the non-image area of the printing plate. If this is not true the ink will adhere, or transfer, to the non-image area of the plate which results in toning. Calculations indicate the preceding conditions are true in conventional offset lithography when the hydrophilic non-image area is wet. When wet, ink adhesion to the plate falls to a point lower than the ink cohesion to itself. In technical terms, it is described as thermodynamic equilibrium. Xerox tested the model and found that there were exceptions when encountered under practical conditions.

The 3M Company referred to the surface energy requirements as the "release value" of an ink. The patent obtained by 3M described the importance of the "ink release value" and how it must be higher for the ink than for the non-image area.[1]

Viscous Flow and The Elastic Release Model. Elasticity is the ability to be stretched. Conventional lithographic inks are complex viscoelastic fluids which exhibit viscous flow behavior in the inking nip. The result is ink film splitting and standing at the nip exit which results in toning in driography. When highly elastic inks are used, viscous flow is minimized and inks can release cleanly, depending on surface energy characteristics. The problem is that if elasticity is too high solid images may not completely fill-in, paper may pick, and general ink flow problems occur in the ink train. Xerox concluded their study by claiming that the elastic release model is only a minimal variable of ink release.[2]

The Weak Fluid Boundary Layer Model. This mechanism is believed by Xerox to be the most reliable explanation of driographic ink release. Basically the model states that ink release will occur if a less viscous layer lays between the ink and the non-image area of the plate. The less viscous fluid may be a vapor or a liquid and the fluid must come from within the ink itself.

The models Xerox described are excellent in the understanding of lithographic ink release theories. Another study by Xerox Corporation involved xerographic toner and driography. The Xerox Corporation apparently had an interest in using xerographic toner for the image area of a driographic plate. The paper concerned itself with adhesion properties of the toner to the silicone rubber base. From these studies, and others done by Xerox in the 1970's, the Xerox Company apparently had intentions of marketing driographic products but have not done so as of this date.[3]

Source material used in background work for this thesis included 33 articles involving driography from the 1970's and 31 articles from the 1980's. Many of these articles were from foreign countries where driography has found more success than in the United States.

Articles included trade journals from Australia, Canada, and America. These articles described driography in the most basic form and made references to production problems which have occurred. It is realized that the indebtedness of trade journals is limited but they indicate the general public's knowledge of driography and some of the actual experiences when put into production.

On 25 April 1978, Toray Industries received a patent from the United States Patent Agency. It is patent number 4,086,093 and is entitled "Dry Planographic Printing Plate".

The patent explains the plates make-up and why certain designs were used. Toray described the background of the invention, the procedures used in developing the plate, and examples of some of their testing methods. The patent helped extensively in understanding driographic principles and in the writing of this thesis.

In 1974, Thomas Rigg, a graduate student at the Rochester Institute of Technology, presented his thesis which involved driography. His thesis is entitled "A Study of the Effect of Ink Tack, Printing Pressure, and Printing Speed on Toning in the Driographic System". Mr. Rigg worked with 3M plates which since have been discontinued on the market. His conclusions indicated that ink tack is a significant factor when dealing with toning in driography. He recommended further research with driography and the amount of toning.

FOOTNOTES FOR CHAPTER 3

[1]U.S. Patent, Dry Planographic Printing Plate, No. 4,086,093, April 25, 1978.

[2]S.L. Gaudioso, "Mechanism of Ink Release in Waterless Lithography", TAGA Conference Proceedings (1975), pp. 177-194.

[3]Ibid

CHAPTER 4

THESIS OBJECTIVES AND HYPOTHESIS

Driographic plates have been available to printers for almost two decades. The basic principle of driography is that by using a material that repels ink for the non-image area of the plate fountain solution is not required to keep this area from printing. With the absence of fountain solution driography avoids many of the limitations and pitfalls of conventional lithography. Initially conventional lithographic inks were used with limited success but with the development of special inks driography has become more appealing to printers. Driography has already established a place in the European printing market. From background research the biggest problem with driography is toning of the non-image area of the plate. This study will investigate some of the variables which affect the degree of toning with special emphasize on ink tack. The plate used in the experiment is Toray's negative working driographic plate.

The hypothesis is that toning in the non-image area of a driographic plate will increase as ink tack decreases. Variables which may effect the degree of toning such as roller pressure, press speed, ambiant temperature, and relative humidity will be monitored and kept constant as possible.

CHAPTER 5

METHODOLOGY

The hypothesis states that as ink tack decreases toning will occur in the non-image area of a driographic plate. Two approaches to test the hypothesis were employed in the experiment. Initially a method to monitor ink tack at the point of impression by recording ink temperature on an inking form roller was conceived. This required a conversion process using an inkometer to convert ink temperature to ink tack. The other method required a tack-reducer to alter the inks tack to the point toning occurred.

The plates used in the experiment were Toray negative working driographic plates. The plates were obtained from the Pittman Company and were exposed and processed according to manufacturers recommendations. The Pittman Company also supplied special driographic ink that they found to be best suited for driographic printing.

The initial approach to prove the hypothesis required a technique to measure temperature on an inking form roller. An electronic thermocouple manufactured by the Fluke Company satisfied this requirement. The device displayed temperature on a digital read out and operated with minimal delay.

An initial press run was performed with a conventional lithographic plate and conventional ink. Ink temperatures were monitored at various times resulting in temperature ranges between 76° to 80°. The press was cleaned between each press run.

The next press run was performed with the driographic plate and the special ink supplied by Pittman. The color came up immediately with waste of only one or two sheets. The driographic plate ran clean throughout press run even when excessive ink was intentionally added. Ink temperatures remained relatively constant at 76° throughout entire press run. Increasing press speed did not drastically alter ink temperature but may have if press was allowed to run longer.

The third press run was performed with the driographic plate and conventional ink. The plate ran clean for a minimal amount of copies (five or six) and began to scum. Ink temperature was recorded at 77° and the plate did not clean up on press once toning occurred. The plate had to be cleaned by hand.

Analyzing the first three press runs, it was realized that another press run was required. Using the same conditions as the second press run, with the driographic plate and the special ink, a fourth press run was performed. The color again came up immediately and the plate ran clean.

To intentionally try to promote toning the paper feed and ink fountain were shut off and the press was allowed to run. After five minutes the press was put back on impression but no toning occurred. The temperature reading at this point was 78°. It was critical to the success of this part of the experiment for the plate to tone.

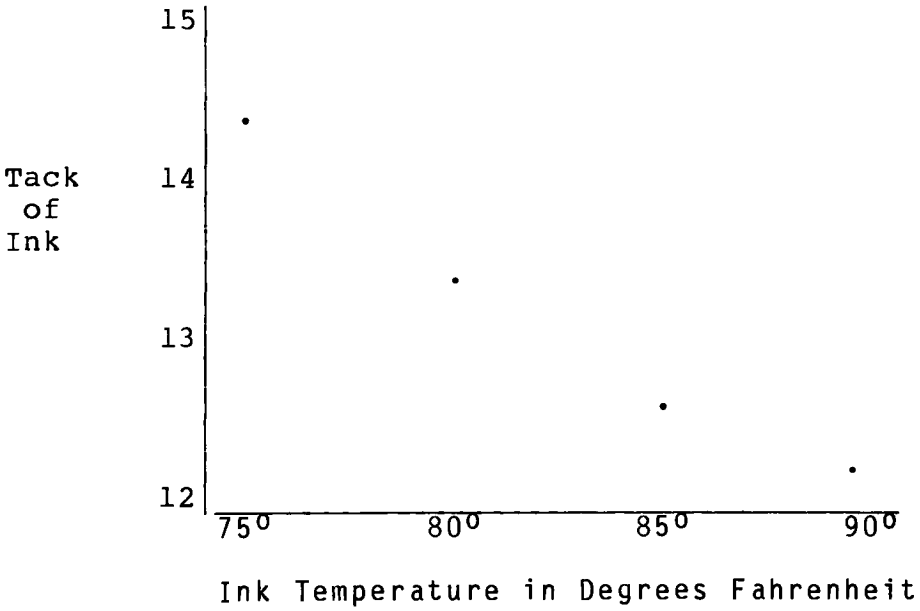
To intentially promote toning a hair dryer was blown directly onto the form roller. After ten minutes there was a significant rise in ink temperature. Plate images began to fill in and the plate had some slight toning. The ink temperature at this point was 90°+.

Upon completion of the press runs the conversion process was performed. Using the inkometer and the thermocouple, ink temperatures were converted to tack readings. The temperature control on the inkometer was adjusted to obtain appropriate ink temperatures. This technique heated the ink on the inkometer to the desired temperature before each tack test. Ink temperatures on the inkometer were confirmed with the thermocouple and the temperature control was adjusted when necessary until desired ink temperature was achieved. The tack readings were recorded and were used to develop the following curves.

CONVENTIONAL LITHOGRAPHIC INK WITH FOUNTAIN SOLUTION

INKOMETER SPEED: 800 RPM

Temperature	Tack
75°	14.2
80°	13.4
85°	12.7
90°	12.3



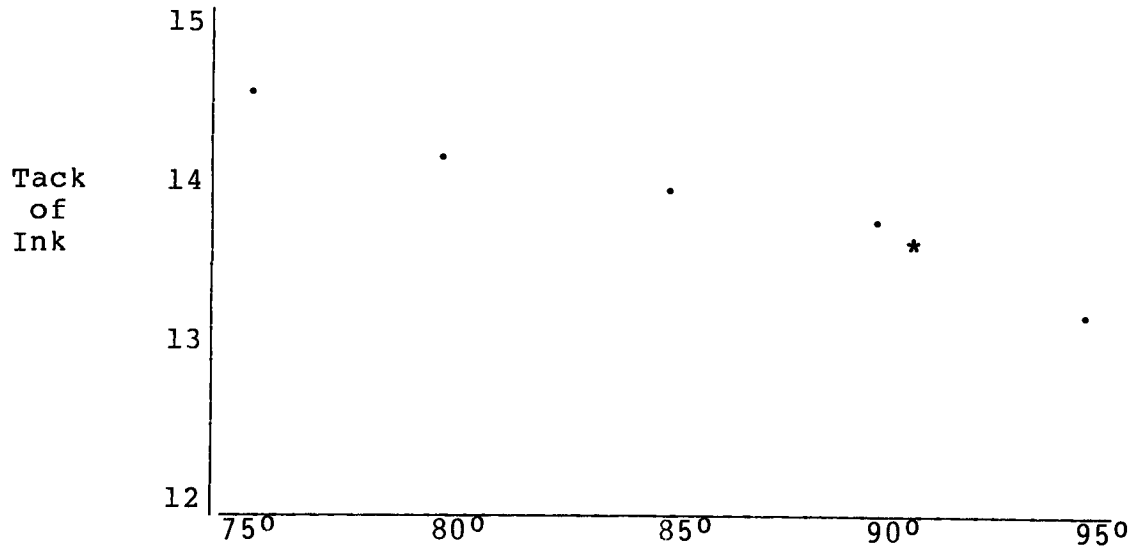
Tack Curve for Conventional Lithographic Ink with Fountain Solution.

FIGURE 2

SPECIAL DRIOGRAPHIC INK

INKOMETER SPEED: 800 RPM

Temperature	Tack
75	14.7
80	14.3
85	14.0
90	13.8
95	13.2



* - Plate images filled in and plate began to tone.

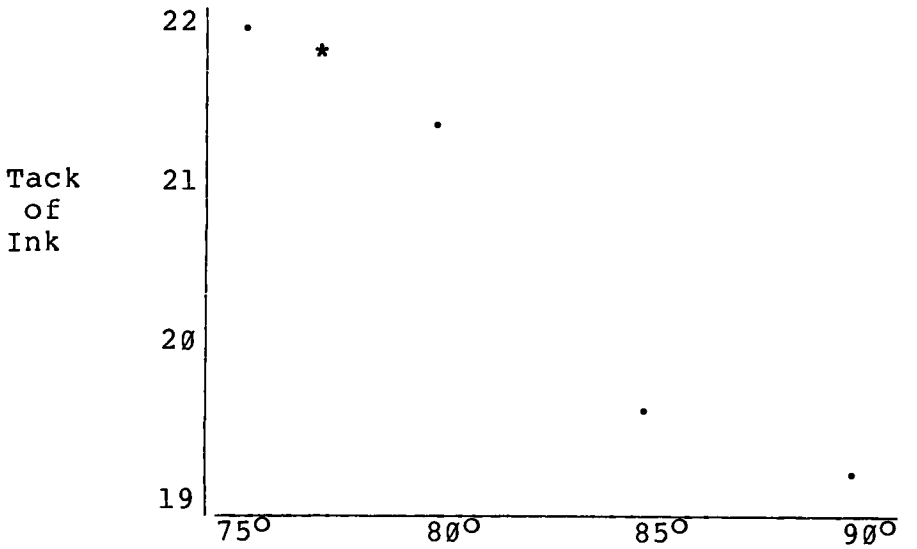
Tack Curve for Special Driographic Ink.

FIGURE 3

CONVENTIONAL LITHOGRAPHIC INK WITHOUT FOUNTAIN SOLUTION

INKOMETER SPEED: 800 RPM

Temperature	Tack
75	22.0
80	21.4
85	19.6
90	19.3



* - Plate toned at 77°

Tack Curve for Conventional Lithographic Ink without Fountain Solution.

FIGURE 4

A second approach to test the hypothesis was performed to support the initial method. Ink tack of the special ink was reduced to various degrees with tack-reducer. Tack-reducer is made from varnishes and is added to lithographic inks under normal conditions to avoid "hickies", "set-off", excessive paper curl, increase ink flow and various other task. Each ink/tack-reducer mixture was run on the press with the driographic plate and the tack was immediately calculated on the inkometer. By lowering the tack a minimal degree toning began to occur. As the tack was reduced more toning increased until the entire plate took on ink.

Test results revealed that at its normal tack of 14.0 the special ink ran cleanly throughout the press run. By dropping the tack to 13.7, the driographic plate began to lightly tone. When tack was lowered to 13.4 toning increased. At a tack of 13.0 the plate completely took on ink. This technique of using tack-reducer may or may not have been an adequate test of the hypothesis depending on whether or not the tack-reducer had an ingredient that had an adverse affect on the driographic process.

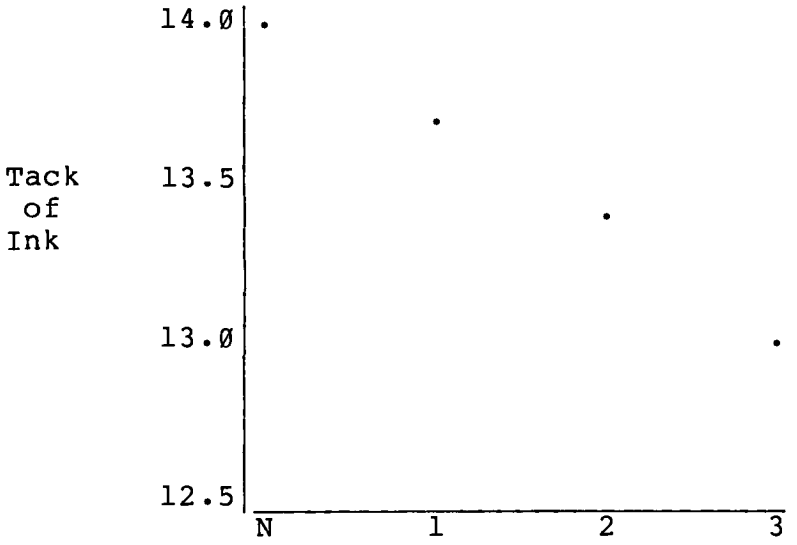
SPECIAL DRIOGRAPHIC INK WITH TACK-REDUCER

N-14.0 - Normal tack of ink without any tack-reducer

Mixture 1 - 13.7 - Plate toned lightly

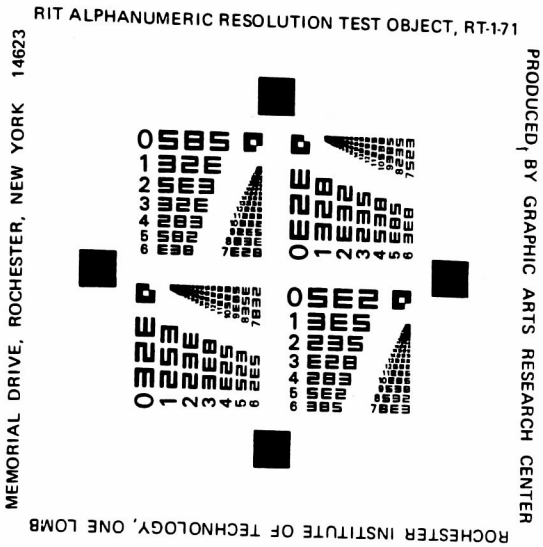
Mixture 2 - 13.4 - Toning slightly increased

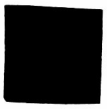
Mixture 3 - 13.0 - Plate completely took ink

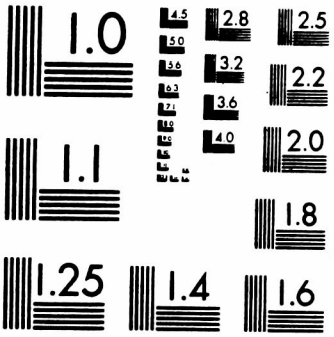


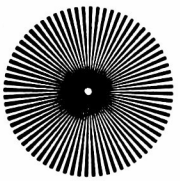
Tack Curve for Special Driographic Ink with Tack Reducer

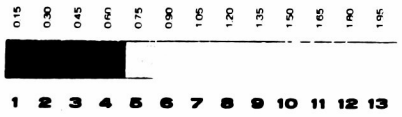
FIGURE 5

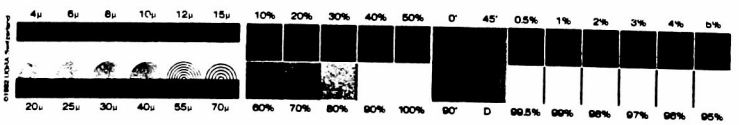






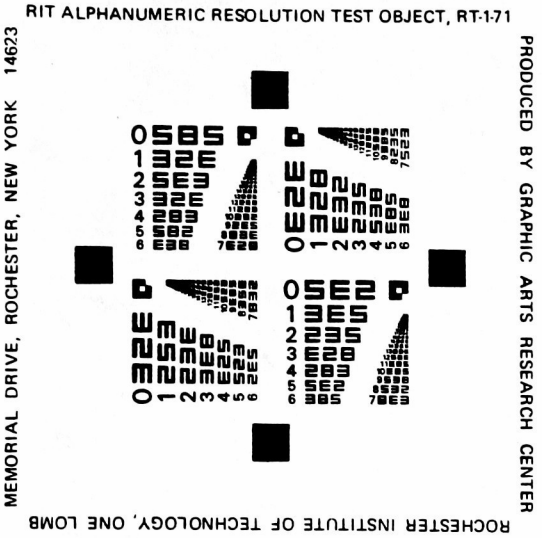


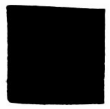


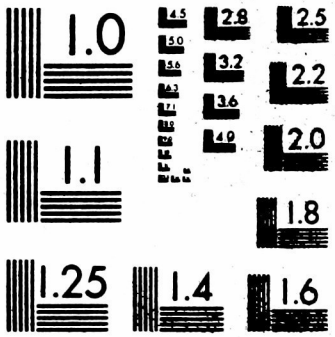


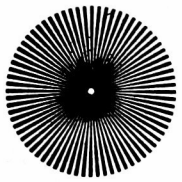
DRIOGRAPHY

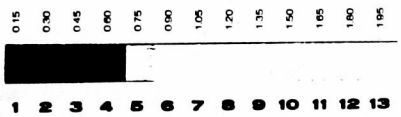
FIGURE 6 - Printed Sample of Driography

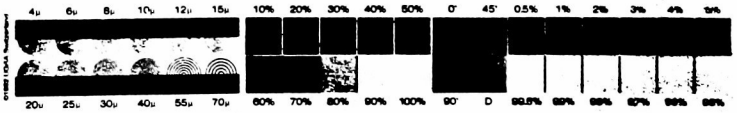












DRIOGRAPHY

FIGURE 7 - Printed Sample of Driography with Slight Toning

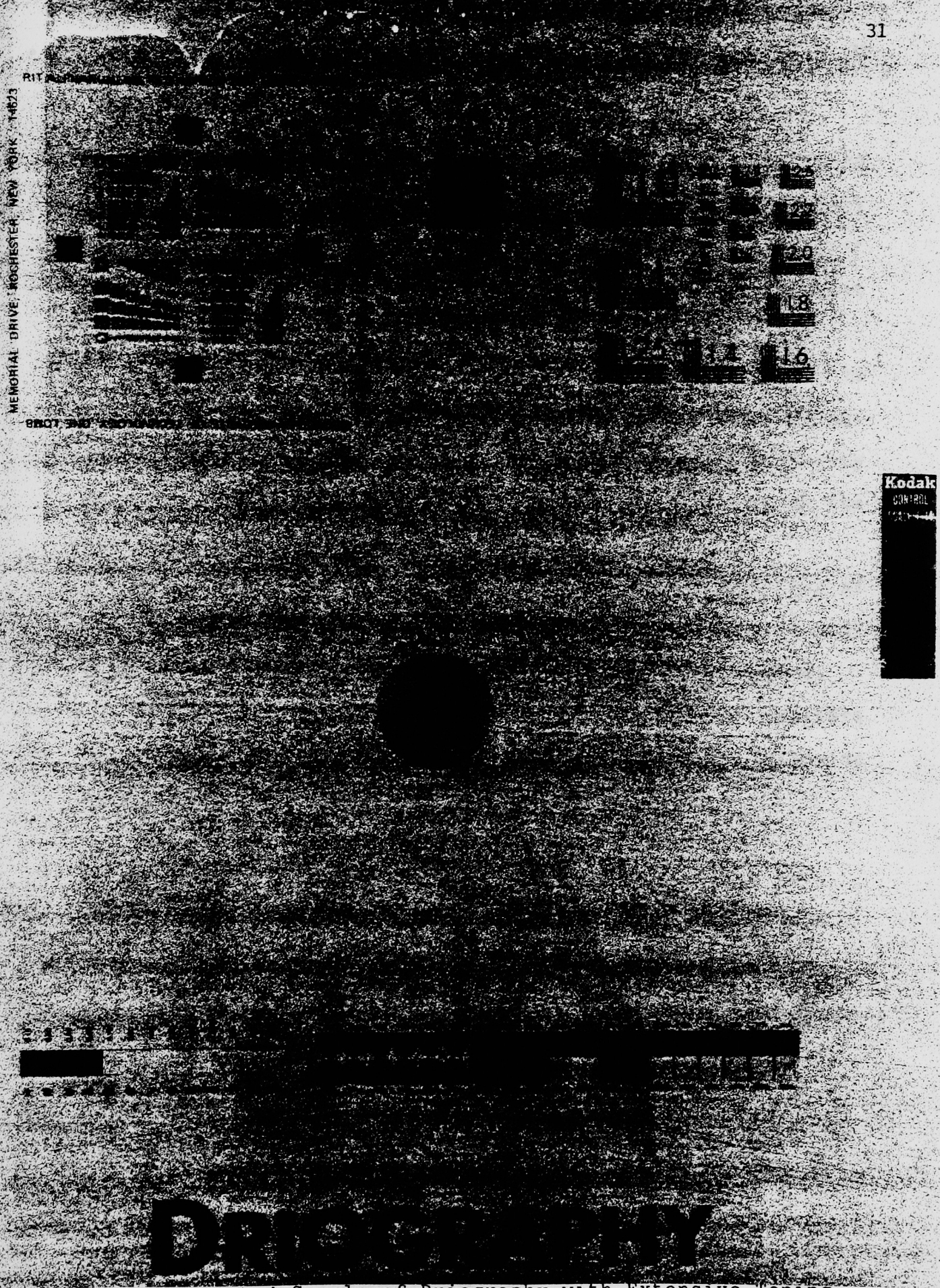


FIGURE 8 - Printed Sample of Driography with Extensive Toning

TEST TARGETS

Test targets are an essential component for accurate and informative testing. The test targets used for this hypothesis were chosen for their attributes as well as their availability at the time of testing. The following test targets were used:

KODAK T-14 CONTROL SCALE: The stepped density scale is designed to maintain proper plate exposure and processing. The scale ranges from a density of 0.04 (step 1) to a density of 2.05 (step 14) in 0.15 increments. A solid step 5 on the plate was held for this test.

STAR TARGET: The target reveals undesirable slurring of images during a press run. Slurring occurs for several reasons and was minimized to assure accurate test results.

UGRA PLATE CONTROL WEDGE: This control wedge monitors plate making and printing. It indicates the following criteria on the plate:

- exposure
- resolving power
- gradation
- halftone dot structure

Printing variables monitored are:

- slurring
- doubling
- tone reproduction

The control wedge consists of five elements:

- Continuous-tone wedge: 13 steps 4x5 mm
- Micro-lines: 12 circular patches, diameter 4.5 mm, positive and negative halves
- Halftone wedge 60 lines/cm (150 lines/in): 10 steps 5x5 mm
- Slur target: 4 steps 5x5 mm
- Small dot patches, negative and positive: 12 steps 5x5 mm

SOLID INK BLOCK: A solid ink area was included to monitor "Solid Ink Density" during press run.

CHAPTER 6

MEANS AND MATERIAL

RIT ALPHANUMERIC RESOLUTION TEST OBJECT

KODAK T-14 PLATE CONTROL SCALE

UGRA PLATE CONTROL WEDGE (PCW)

STAR TARGET

IMAGE ASSEMBLY MATERIALS

TORAY NEGATIVE WORKING DRIOGRAPHIC PRINTING PLATES

CONVENTIONAL LITHOGRAPHIC PLATE (WESTERN)

PLATE EXPOSURE UNIT

PLATE PROCESSOR CHEMISTRY

DUPLICATOR PRINTING PRESS (A.B. DICK)

SPECIAL DRIOGRAPHIC INK (BLACK)

CONVENTIONAL LITHOGRAPHIC INK (BLACK)

FOUNTAIN SOLUTION (SEA MIST)

UNCOATED PAPER

INK TACK REDUCER

FLUKE ELECTRONIC THERMOCOUPLE

THWING-ALBERT ELECTRONIC VISCOMETER

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSION

This study investigates the hypothesis that ink tack has an affect on the degree of toning on a driographic plate.

It can be concluded that if proper ink is used, a driographic plate will run cleanly. By applying hot air directly to the inking form roller ink tack lowered to the point toning occurred. Also by intentionally lowering ink tack with tack-reducer toning occurred. From these tests results it could be concluded the hypothesis stands true. But with further inquiry and some deductive reasoning it appears the hypothesis does not completely resolve the mechanism required for proper ink release in the non-image area of a driographic plate.

When the special driographic ink was permitted to run as intended, the plate ran excellent as proven in the second press test. The desired ink density was acquired within a few sheets and the test targets printed clearly.

The key to the success of driography is the special driographic ink. To investigate the composition of the ink a local ink company, which had previous experience with driography, was contacted. They indicated the special ink requires a complex varnish formula with a limited percentage of plasticizing oils and specific resins. The ink manufacture

also indicated it was important to have as little oil in the ink as possible. They concluded the ink formulation was proprietary but when confronted revealed additional silicone oil was not involved.

The ink manufacturer emphasized the importance of as little oil in the ink as possible. If it is the amount of oil and not the ink tack that causes toning certain phenomena that occurred during the experiment can be explained. First, the fact that when a conventional ink with a tack extremely higher than the special driographic ink was used, the driographic plate almost immediately scummed or toned up. Also, when the ink was heated with a blow dryer to intentionally promote toning it took a big rise in ink temperature before the plate background was affected. The hot air lowered ink viscosity causing images to fill in long before any toning occurred and then the toning was only slight. This could be partly due to the evaporation of ink oils by the blow dryer allowing ink temperature to raise and tack to lower before the plate background was affected. Finally, if oil is detrimental to toning then it would explain why adding a minimal amount of tack reducer, which is quite oily, to the special ink immediately resulted in toning. It can be concluded that contrary to the hypothesis it is not necessarily the ink tack, but rather the percent of oil in the ink, which promotes toning in the non-image area of a driographic plate.

A cost study program was not performed but the current price listing from Pittman indicated that there was not a substantial difference between driographic plates and conventional lithographic plates. Any additional plate cost should be retrieved with less paper spoilage, quicker makeready, and the elimination of fountain solution.

RECOMMENDATIONS

By emphasizing the importance of as little oil in the ink as possible, the ink manufacture was contradicting the basis of the hypothesis. Upon reflection, it may be the excess oil in the ink which prevents adequate back trapping of ink in the non-image area. It is recommended further study be conducted with different ink formulations for driography applications.

The test targets used were not an integral part of the experiment. They did reveal the fine detail a driographic plate could reproduce as claimed by the manufacture. With the capability to reproduce fine detail and with the increased interest by the public for higher screen rulings and special screens the use of driography may suit special plate requirements. Driographic plate would be ideal for 200 plus line screens and special application screens such as the Random Microlenticular Screen (RML) which is claimed to be equivalent to a 600 line screen and is used for mapping and quality art reproductions.

One last recommendation which does not directly concern driography involves ink testing. In performing driographic testing ink tack was of great concern. It appeared the methodology was correct in assuming temperature has a direct relationship to ink tack but no documentation was available. Further research into the relationship ink temperature, viscosity, and tack have with each other would support future research.

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APPENDIX

U.S. PATENT FOR DRY PLANOGRAPHIC PLATE

United States Patent [19]

Enomi et al.

[11] 4,086,093

[45] Apr. 25, 1978

[54] DRY PLANOGRAPHIC PRINTING PLATE

[75] Inventors: Yuh Enomi, Kyoto; Masaharu Kobayashi; Takashi Kubota; Yoichi Shimokawa, all of Otsu, all of Japan

[73] Assignee: Toray Industries, Inc., Tokyo, Japan

[21] Appl. No.: 713,576

[22] Filed: Aug. 11, 1976

Related U.S. Application Data

[63] Continuation of Ser. No. 514,063, Oct. 11, 1974, abandoned.

[51] Int. Cl.[2] G03G 1/08

[52] U.S. Cl. ..... 96/86 P; 96/114; 96/115 R; 96/35.1

[58] Field of Search ..... 96/86 P, 115 R, 114

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Primary Examiner—John D. Welsh

Attorney, Agent, or Firm—Miller & Prestia

[57] ABSTRACT

A laminated negative acting presensitized planographic printing plate for use in dry planography having

(a) a base layer,

(b) a silicone rubber layer overlying the base layer, and

(c) a photoadhesive layer overlying the silicone rubber layer comprising at least one photopolymerizable unsaturated compound having a boiling point above 100° C and a photoinitiator.

Under exposure to light through a negative transparency, the photoadhesive layer polymerizes in the exposed image area and adheres to the underlying silicone rubber layer, while remaining non-adhesive to the underlying silicone rubber layer in the unexposed non-image area.

The unexposed photoadhesive layer only is removed to bare the underlying silicone rubber layer which is made an ink-repellent non-image area and the photoadhesive layer remaining in the exposed area is made an ink-receptive image area.

The surface of the photoadhesive layer accepts ink from inking rollers, while the silicone rubber background area will not remove ink from the rollers and thus remains ink free.

16 Claims, No Drawings

DRY PLANOGRAPHIC PRINTING PLATE

This is a continuation of application Ser No. 514,063, filed Oct. 11, 1974 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a negative-type planographic printing plate having ink-repellent silicone rubber in a non-imaged area and is capable of printing in the absence of dampening.

Heretofore, several proposals have been made with reference to a dry planographic plate having an ink-repellent layer of silicone rubber, all of which, however, have various deficiencies such as having inferior strength of the printing plate or presenting problems in developing method. For example, what is disclosed in Japanese patent publication No. 2361/1972 is a presensitized planographic printing plate providing a photo-insolubilizable water soluble diazonium resin layer on the layer of silicone rubber. When a negative transparency is put on said plate and exposed to light and thereafter treated with aqueous developing liquid, the diazonium resin layer in the unexposed area dissolves to expose the surface of the silicone rubber layer to form an ink-repellent non-imaged area, whereas in the exposed area, the hardened diazonium resin layer remains to form an ink-receptive image area. However, there is insufficient adhesion between the diazonium resin layer in the image area and the underlying silicone rubber layer, and this deficiency of the planographic printing plate is such that the diazonium resin layer of the image area is peeled by inking rollers during printing or is removed by careless scratch.

An object of the present invention is to overcome such deficiencies and to provide a negative-type planographic printing plate excellent in adhesive strength of the ink-receptive image area, surface strength of the printing plate, storability, scratch resistance and high durability in long run printing.

Another object of the present invention is to provide a negative-type planographic printing plate having excellent reproducibility of image and broad permissible range of the exposing time.

SUMMARY OF THE INVENTION

The presensitized dry planographic printing plate in the present invention is a negative acting plate comprised of

(a) a base layer,

(b) a silicone rubber layer overlying the base layer, and

(c) a photoadhesive layer overlying the silicone rubber layer, comprising at least one photopolymerizable unsaturated compound having a boiling point above 100° C and a photoinitiator.

Upon exposure to light through a negative transparency, the photosensitive layer in the exposed image area polymerizes and adheres firmly to the underlying silicone rubber layer, whereas the photoadhesive layer in the unexposed non-image area remains non-adhesive to the underlying silicone rubber layer.

Next, a planographic printing plate is produced in which the photoadhesive layer is removed only in the unexposed area to bare the underlying silicone rubber layer, the photoadhesive layer remaining in the exposed area is made an ink-receptive image area and the silicone rubber layer in the unexposed area is made an ink-repellent non-image area

The present invention has the following novel and important characteristics Upon irradiating actinic light through a negative transparency to the printing plate the photoadhesive layer in the exposed area not only polymerizes and cross-links to become insoluble, but also adheres to the underlying silicone rubber layer and cannot be easily peeled off. As a result, the adhesive strength of the ink-receptive image area of the resulting printing plate and eventually the strength of the plate surface is increased remarkably, and not only are the storability and scratch resistance improved, but also the durability in long-run printing is strikingly increased ! this case photoadhesion in the interface between the photoadhesive layer and the silicone rubber layer has a very important significance, which is remarkably different from the hitherto known cases.

The flexible base substrate employed in the present invention should be sufficiently flexible for mounting on a lithographic press and strong enough to withstand the load normally produced by the lithographic press. Representative substrates include coated paper, metals or plastics such as polyethylene terephthalate. However, it is most preferable to use a substrate whose reflectivity to light of a wave length of 300 - 400mμ is not more than 20%, since the reproducibility of the image is thereby strikingly improved. In case such halation-preventing substrate is used, the permissible range of the exposure time (the width of proper exposure time) is broadened and possible to obtain a sharp image relief from highlights to shadows.

The fact that a halation-preventing substrate develops such great effect in a planographic printing plate without requiring water having a photosensitive resin layer on a silicone rubber layer was not recognized in the prior art. It is well known to provide a halation-preventing layer beneath a photosensitive resin layer upon applying a photopolymerizable resin to the production of ordinary relief and lithographic printing plates. However, the present invention is entirely different in structure from the known cases in that a halation-preventing layer is provided beneath a silicone rubber layer supporting a photosensitive resin layer.

If, as in the prior art, a halation-preventing layer is provided between a photoadhesive layer and a silicone rubber layer photoadhesion is not realized and a photoinsolubilized relief easily peels from the silicone rubber layer. The superiority of a halation-preventing base substrate beneath the silicone rubber layer as in the present invention is thus readily understood.

The halation-preventing base substrate used in the present invention has adequate flexibility for mounting on an ordinary lithographic press and is strong enough to readily withstand the load normally produced by the lithographic press. As illustrative of such base substrates, the following may be cited:

(1) a metal plate, paper or a plastic sheet provided with a halation-preventing layer on the surface,

(2) a substantially transparent plastic film provided with a halation-preventing layer on the back surface, and

(3) paper and plastic film impregnated with or having dispersed therein an ultraviolet light absorbing agent.

Following is a list of effective ultraviolet light absorbing agents. These ultraviolet light absorbing agents may be dissolved or dispersed in solutions of various poly-

me. binders a. ? applied to the base substrate to thereby provide halation-preventing layers.

(1) benzophenone derivatives: 2,2'-dihydroxy-4-methoxy benzophenone, 3-chloro-2-hydroxy benzophenone, 4,4'-dimethylamino benzophenone or "Light Absorber DBR" manufactured by Dow Chemical Co. of U.S.A.

(2) benzotriazol derivatives: "Tinuvin P", 2-(2'-hydroxy-5'-methyl-phenyl)-benzotriazol and "Tinuvin 320", ingredients not made public manufactured by Geigy Ltd. of Switzerland.

(3) phenyl salicylate and derivatives thereof: 4-t-butylphenyl salicylate and 4-octylphenyl salicylate.

(4) acrylonitrile derivatives: "Ubinul N-35", ethyl 2-cyano-3,3-diphenylacrylate, and "Ubinul 330", N-539",2-diethylhexyl-2-cyano-3,3-ciphenyl acrylate, manufactured by Antala Chemical Co. of U.S.A.

(5) other commercially available ultraviolet light absorbing agents, such as: "Inhibitor-HRT" "HPT," hexamethyl phosphoric triamine, manufactured by Eastman Chemical Co. of U.S.A., "Stouffer Stabilizer-UV928" and "Stouffer Stabilizer-UV1261", the ingredients of both of which are not made public, manufactured by Stouffer Chemical Co. of U.S.A. as well as "C1729" and "AM101", the ingredients of both of which are nickel bisoctyl phenyl sulfide, manufactured by Ferro Chemical Co. of U.S.A.

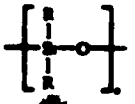
(6) yellow and red conventional inorganic and organic pigments, the Colour Index numbers for which are as indicated: Orange Lake CI 77199, Molybdenum Orange, Cadmium Yellow, Yellow Lead, CI 77600 Lead Chromate CI 77601, Hansa Yellow CI 11670, Chromium Vermillion, CI 77605, Red Lead CI 77578, Lake Red C CI 15585, Chromium Red, Red Iron Oxide CI 77491, Washing Red, Bon Maroon CI 77766, Vermillion, etc.

For the purpose of improving adhesion between such halation-preventing base substrates and a silicone rubber layer, it is preferable to apply a thin (0.05 - 1.0μ) coating of silicone primer (surface treating agent) to the surface of said substrate.

As silicone primers used for such purpose, besides commercially available primers such as "SH 4094", "SH 1200" and "SH 1201", silane coupling agents such as "SH 6020", "SH 6040" and "SH 6075" may be cited, all manufactured by Toray Silicone Co. of Japan.

The thickness of the silicone rubber layer used in the present invention is not particularly critical, and is useful in the normal range of 0.5 - 50μ, and preferably 1 - 10μ.

Useful silicone rubber is obtained by sparsely cross-linking a linear diorganopolysiloxane (preferably dimethyl polysiloxane) which is a base polymer. The density of this cross-linking may be expressed by an R/Si ratio in the following formula, and in useful silicone rubber, such density is within the range of 1.95 - 2.10, preferably 1.99 - 2.01. A representative silicone base polymer has the following repeating unit



wherein a is an integer not less than 2, R stands for an alkyl, halogenated alkyl, vinyl aryl or cyanoalkyl group having 1 - 10 carbon atoms, it being preferable that at least 60% of R is methyl group.

Useful silicone rubber in the present invention is obtained by condensation reaction of such silicone base polymer and the following silicone cross-linking agent

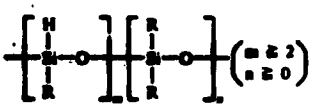
(1) R [illegible]

(2) R [illegible]

(3) R [illegible]

wherein R has the same meaning as mentioned above, R' stands for an alkyl such as methyl and ethyl and Ac stands for acetyl group.

Other useful silicone rubbers may be obtained by reaction of the aforesaid base polymer with H-type silicone oil having the following repeating unit or addition reaction of the aforesaid base polymers in which about 3% of R is vinyl group, or reaction between said H-type silicone oils.



R has the same meaning as mentioned above.

In order to obtain silicone rubber by such cross-linking reaction, besides the aforesaid components, an organometallic carboxylic acid salt of a metal such as tin, zinc, cobalt, lead, calcium and manganese, for example, dibutyl tin laurate, stannic octoate and cobalt naphthenate or a catalyst like chloroplatinic acid is added.

In order to improve the tenacity of silicone rubber and obtain silicone rubber which can withstand frictional force produced during printing, it is possible to mix a filler with the silicone rubber. Silicone rubber premixed with a filler is commercially available as silicone rubber stock or silicone rubber dispersion. In case it is preferable to obtain silicone rubber film by coating as in the present invention, RTV or LTV silicone rubber dispersion is preferably used. As examples of such silicone rubber dispersions, there are silicone rubber dispersions for paper coating such as "Syl off 23," "SRX-257" and "SH-237" manufactured by Toray Silicone Co., Ltd. of Japan.

In the present invention, by incorporating a small amount of photosensitizer in the silicone rubber layer in addition to the aforementioned components, the effectiveness is greatly enhanced. By using such silicone rubber composition, the photoadhesion between the silicone rubber layer and the photoadhesive layer is remarkably increased and it very conveniently provides for achieving the object of the present invention. As such photosensitizer for incorporation in the silicone rubber layer, it is possible to use the same photosensitizer (photoinitiator) which will be contained in a photoadhesive layer to be mentioned later. Most particularly, aromatic ketones, especially benzoin alkylethers are conveniently used. As representative examples of such benzoin alkylethers, there may be cited benzoin ethyl ether, benzoin isopropyl ether and benzoin butyl ether. Amounts to be contained of these photosensitizers are normally 0.1 - 10% by weight based on the total weight of the silicone rubber layer.

The thickness of a photopolymerizable adhesive layer used in the present invention is not particularly limited, but is normally within the range of 0.5 - 50μ, and preferably 1 - 10μ.

The following is the composition of such a photopolymerizable adhesive layer:

(1) at least one kind of photopolymerizable unsaturated compound having a boiling point above 100° C
5.0 - 99.9 parts by weight
(2) photoinitiator
0.1 - 10.0 parts by weight
(3) heat polymerization inhibitor as occasion demands
0.001 - 0.1 part by weight
(4) polymer or inorganic powder as filler for maintaining the dimensional stability of a photoadhesive layer as occasion demands
0.01 - 90.0 parts by weight.

The photopolymerizable unsaturated compound referred to herein means photopolymerizable unsaturated monomers and oligomers.

As such monomers and oligomers, various compounds may be used. However, it is preferable to make at least one kind of such compound a monomer or oligomer containing at least one hydroxyl group and at least one acryloyl or methacryloyl group in the same molecule. It is especially preferable to make the total concentration of the hydroxyl group and the total concentration of the acryloyl group or methacryloyl group in the photoadhesive layer at least 0.1 mmol/g, respectively. The upper limits of these total concentrations are about 15 mmol/g, respectively.

By using such monomer or oligomer, the outstanding improvement provided by the present invention in the aforesaid characteristics of adhesive strength of the ink-respective image area, scratch resistance and high durability in long run printing, is most effectively realized.

This fact becomes more evident upon comparison with a case in which the total concentration of the hydroxyl group and the total concentration of the acryloyl and methacryloyl groups are less than 0.1 mmol/g, respectively. Although photosolubilization may be achieved in such case, the adhesion to the surface of the underlying silicone rubber is inadequate in that the frictional forces generated during development prevent the formation of the relief of the image area, or even if the relief is formed it simply peels when it is lightly rubbed with the finger tip.

The following compounds may be cited as examples of the aforesaid monomer or oligomer containing at least one hydroxyl group and at least one acryloyl or methacryloyl group in the same molecule:

(1) (metha)crylic acid partial ester of a polyhydric alcohol containing 2 - 12 carbon atoms,
(2) addition product of active hydrogen compounds having 1 - 12 carbon atoms such as alcohols, thiols, amines, carboxylic acids, sulfonic acids, phenols, phosphoric acids or hydrogen halide with glycidyl (metha)crylate,
(3) addition product of monoepoxy or polyepoxy compound having 2 - 14 carbon atoms with (metha)crylic acid,
(4) ester of N-methylol(metha)crylamide and oxycarboxylic acid having 2 - 10 carbon atoms,
(5) addition product of N-methylol(metha)crylamide with monoepoxy or polyepoxy compound having 2 - 12 carbon atoms.

Of such monomers and oligomers, those having at least 2 acryloyl or methacryloyl groups and at least 1 alcoholic hydroxyl group are preferable and those having at least 2 acryloyl or methacryloyl groups and at least 2 alcoholic hydroxyl groups are most preferable.

Compounds of the aforesaid monomers and oligomers that are especially useful will be listed below, some of which may be used as raw material for oligomers useful in the present invention:

(1) (metha)crylic acid partial esters of ethylene glycol, propylene glycol, glycerol, sorbitol, trimethylol methane, trimethylol ethane, trimethylol propane and pentaerythritol,
(2) adducts of glycidyl (metha)acrylate with hydrogen chloride, methanol, ethanol, ethylene glycol, trimethylol methane, pentaerythritol, ethanol amine, triethanol amine, ethane dithiol, methylamine, ethylenediamine, xylylenediamine, aniline, phenylenediamine, acetic acid, (metha)crylic acid, malonic acid, succinic acid, maleic acid, fumaric acid, itaconic acid, malic acid, tartaric acid, citric acid, phenol, thiophenol or hydroquinone,
(3) addition products of glycidyl ester having at least 2 1 epoxy groups and 9 - 14 carbon atoms with (metha)crylic acid, for example, addition product of (metha)crylic acid with glycidyl esters of phthalic acid, tetrahydrophthalic acid, succinic acid, adipic acid, maleic acid, fumaric acid or itaconic acid.
(4) diester of N-methylol(metha)crylamide with malic acid, tartaric acid, and citric acid,
(5) addition product of N-methylol (metha)crylamide with glycidyl ester of (metha)crylic acid, phthalic acid, tetrahydrophthalic acid, maleic acid, fumaric acid or itaconic acid.

Aside from the aforementioned (metha)crylic monomers having alcoholic hydroxyl groups, it is possible to cause other ethylenically unsaturated monomers to co-exist as occasion demands. However, whatever monomers are added, it is preferable that the concentrations of (metha)cryloyl group and hydroxyl group as a photoadhesive layer composition be kept above 0.1 mmol/g.

It is possible to cause other photopolymerizable monomers or oligomers to co-exist in the photoadhesive layer an occasion demands and as representative examples of such monomer or oligomer, there may be cited a (metha)crylic acid ester or (metha)crylamide having a boiling point above 100° C derived from a monohydric alcohol or monovalent amine having not more than 30 carbon atoms or (metha)crylic acid ester or (metha)crylamide having a boiling point above 100° C derived from a polyhydric alcohol or polyvalent amine having not more than 80 carbon atoms, the representative examples of such compounds being as follows:

(1) (metha)crylic acid ester of the following alcohols: methanol, ethanol, propanol, pentanol, cyclohexanol, octanol, undecanol, bornyl alcohol, polymethylene glycol, ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, glycerol, trimethylol methane and pentaerythritol,
(2) (metha)crylamide derivatives shown below: (metha)crylamide, N-methylol(metha)crylamide, N-methoxymethyl(metha)crylamide, methylene bis-(metha)crylamide, hexamethylene bis-(metha)crylamide, diacetoneacrylamide and dihydroxymethyldiacetoneacrylamide.

As representative examples of the photoinitiator which may be used in the present invention, the following compounds may be cited:

(1) Benzophenone derivatives such as, for example, benzophenone, Michler's ketone, xanthone, anthrone, etc.,

(2) benzoin derivatives such as, for example, benzoin, benzoin methyl ether, benzoin ethyl ether, etc.,

(3) quinones such as, for example, p-benzoquinone, β-methylanthraquinone, etc.

(4) sulfur compounds such as, for example, dibenzyl disulfide, di-n-butyl disulfide, etc.

(5) azo or diazo compounds such as, for example, 2-azo-bis-isobutyronitrile, 1-azo-bis-cyclohexane carbonitrile, p-diazobenzylethylaniline, Congo Red, etc.

(6) halogen compounds such as, for example, carbon tetrabromide, silver bromide, α-chloromethylnaphthalene, etc.

(7) peroxides such as, for example, benzoyl peroxide, etc.

(8) uranyl salts such as, for example, uranyl nitrate, etc.

It is possible to select most suitable photoinitiators by taking into account the miscibility with other components of a photoadhesive layer and the spectrum of the light source used for exposure. Generally, the following photoinitiators are most preferable:

Benzophenone, Michler's ketone, xanthone, benzoin methyl ether, dibenzyl disulfide and uranyl nitrate

In addition to the aforementioned components it is useful to add a small amount of heat polymerizable inhibitor to the photoadhesive layer for the purpose of improving the storability of the printing plate. As representative examples of such heat polymerization inhibitor, hydroquinone, phenothiazine, 2,4-dinitrophenol and triphenylmethane may be cited. It is also possible to add a dye such as Crystal Violet Powder to the photoadhesive layer so that an exposed area is easily visually discriminated.

Further, it is also possible to mix inorganic powder or polymer with the photoadhesive layer as occasion demands for the purpose of imparting dimensional stability to the photoadhesive layer and improving adhesion to the silicone rubber.

The printing plate so produced achieves improvement in the storability, scratch resistance and durability of the printing plate in long run printing.

On the other hand, these additives tend to cause lowering of the concentration of the (metha)crylic monomer having the hydroxyl group, which is indispensable for the photoadhesive layer.

Because of such possible adverse effects in the present invention it is preferable to so control the weights of the additives as to keep the molar concentrations of (metha)cryloyl group and hydroxyl group derived from a (metha)crylic monomer more than 0.1 mmol/g as the photoadhesive layer composition.

Suitable inorganic powders may usefully be dispersed in the photoadhesive layer and as representative examples of such powders, colloidal silica, calcium carbonate and titanium dioxide may be cited.

A polymer to be added must have properties of ability to mix uniformly with other components of the photoadhesive layer, namely, the monomer, oligomer and photoinitiator in a solution or molten state. The desired composition must dissolve or swell in the developing liquid and must be easily removed in the developing step. The following polymers and copolymers may be used as the desired polymers provided they have such properties. It is possible to mix these polymers and copolymers in the usual manner an occasion demands and use the resultant mixtures.

(1) Vinyl polymers or (metha)crylic acid, (metha)crylic acid ester polymers and copolymers thereof.

For example, polymers such as polyvinyl alcohol, polyvinyl formal, polyvinyl butyral, or polymers or copolymers of vinyl acetate, vinyl chloride, ethylene, vinyl methyl ether, styrene, (metha)crylic acid, methyl-, ethyl-, cyclohexyl-, benzyl-, 2-ethylhexyl-, glycidyl-, 2-hydroxyethyl-, 2-hydroxypropyl-, 3-chloro-2-hydroxy-propyl- and dimethylaminoethyl-, 2-acid-phosphoxy-ethyl-, 3-chloro-acid-phosphoxyethyl (metha)crylates, and (metha)crylamide, N-methylol(metha)crylamide, N-methoxybutyl(metha)crylamide, hydroxymethyldiacetoneacrylamide, 2-acrylamido-2-methylpropane sulfonic acid.

(2) Unvulcanized rubber such as, for example, natural rubber, polybutadiene, polyisobutylene, polychloroprene, polyneoprene or copolymers thereof.

(3) Polyethers such as, for example, polyethylene oxide and polypropylene oxide.

(4) Polyamides such as, for example, copolymers of the following monomers: caprolactam, laurolactam, hexamethylenediamine, 4,4'-bis-aminocyclohexylmethane, 2, 4, 4-trimethylhexamethylenediamine, isophoronediamine, diglycolic acid, isophthalic acid, adipic acid, sebacic acid, etc.

(5) Cellulose derivatives such as, for example, cellulose acetate, methylcellulose, carboxymethylcellulose, hydroxypropylcellulose, etc.

(6) Polyesters such as, for example, condensation products of phthalic anhydride, maleic anhydride, bis-phenol A, ethylene oxide and propylene oxide.

(7) Polyurethane such as, for example, polyurethane of hexamethylene diisocyanate, toluene diisocyanate and naphthalene 1, 5-diisocyanate with 1, 4-butanediol.

(8) Prepolymers of epoxy, urea, alkyd, melamine and phenol resins.

(9) Gum rosin, polyterpene, and cumarone - indene resin.

(10) Other polymers such as, for example, gum arabic and gelatin.

These polymers are selected in combination with the kind of developing liquid used. However, the following compounds are especially useful:

A polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, copolymer of (metha)crylic acid and/or maleic acid, fumaric acid, itaconic acid (0 - 20 parts by weight) - methyl methacrylate and/or styrene (0 - 50 parts by weight) - (metha)crylic acid ester having 5 - 20 carbon atoms and/or vinyl acetate (20 - 100 parts by weight), or copolyamides of nylon 6 - nylon 66 - 2, 2, 4-trimethylhexamethylene diamine 6 (1:1:1 by weight) or nylon 6 - nylon 66 - 4, 4'diaminocyclohexylmethane 6 (1:1:1 by weight).

As explained above, the base substrate, the silicone rubber layer and the photoadhesive layer are indispensable elements of a planographic printing plate according to the present invention. However, the surface of the so constituted planographic printing plate is somewhat tacky, tending to cause dust to adhere thereto and thereby posing the problem that a negative transparency is unlikely to adhere sufficiently close to said surface in the exposure step. It may therefore be desirable

to interpose a thin transparent protecting film or to form a protecting layer on the surface of the photoadhesive layer using a polymer solution. This protecting film also plays a role of inhibiting osmosis (permeation) of atmospheric oxygen into the photoadhesive layer and promoting photopolymerization of the photoadhesive layer. Such protecting film is useful in the exposure step, but it is obvious that the protecting film is removed by peeling or dissolution in the developing step and is unnecessary in the printing step.

Useful protecting films have transparencies capable of transmitting ultraviolet light (ray) having a wave length of 300 - 400mμ and a thickness below 50μ, preferably below 10μ. As representative examples of such useful films layers, the following plastics may be cited:

Polyethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, polyethylene terephthalate and cellophane.

As explained above, a planographic printing plate as a laminate according to the present invention may be produced, for example, by the following three methods:

(1) To the base substrate, a silicone rubber dispersion is applied using ordinary coaters such as reverse roll coater, air knife coater and Mayerbar coater. In this case, it is possible to pretreat the base substrate with silicone primer. Next, the solution of a photoadhesive layer composition is applied to the silicone rubber layer by the same method used in applying the silicone rubber dispersion. In applying this solution it should not disturb the smooth surface of the silicone rubber layer. It is possible to add a paint additive of the silicone series or a surface active agent of the fluorine series to said solution for producing a uniform coating of said solution as occasion demands.

(2) On a peelable carrier sheet, for example, polyethylene, polypropylene and polyethylene terephthalate films, metal sheets, or silicone coated releasing paper or films, a photoadhesive layer is formed. The aforesaid photoadhesive layer formed on the peelable carrier sheet is caused to adhere closely onto a silicone rubber layer provided on the base substrate by the same method as in (1) above. In this case, it is possible to pretreat the surface of said photoadhesive layer with silicone primer.

(3) A silicone rubber dispersion is applied to a photoadhesive layer provided on a peelable carrier sheet by the same method as in (2) above, and sufficiently dried. Additionally, a base substrate is treated with silicone primer and is caused to closely adhere to the silicone rubber layer produced previously.

The peelable carrier sheets of (2) and (3) above, may be made protecting films per se, but it is also possible to paste on new protecting films after peeling said carrier sheets. Similar good photosensitivity may be obtained using the plate without protecting film, if exposure is made after the plate is stored in an atmosphere of gases like nitrogen and carbon dioxide to expel the dissolved oxygen of the photoadhesive layer.

As a method of providing the protecting film, besides the aforesaid film lamination, it is possible to use a method of applying a polymer solution like polyvinyl alcohol onto the surface of the photoadhesive layer or applying said polymer solution onto the peelable carrier sheet to form an oxygen transmission preventing layer in advance, applying the photoadhesive layer thereon and peeling the peelable carrier sheet at a time when lamination of the silicone rubber layer and the base substrate is complete.

The planographic printing plate of the present invention produced as described in the foregoing, is exposed to actinic light through a negative transparency closely adhered to said plate in vacuo. The light source used for this exposure step should generate abundant ultraviolet rays (light), and mercury lamps, carbon arc lamps, xenone lamps, metal halide lamps or fluorescent lamps may be used as such light source.

In the printing plate which has been exposed to light, not only does the photoadhesive layer of the exposed area harden by photopolymerization cross-linking reaction, but it also adheres strongly to the underlying silicone rubber layer. Therefore, depending upon the kind of the protecting film and the composition of the photoadhesive layer, when the protecting film is peeled after exposure, the photoadhesive layer of the unexposed area peels together with the protecting film and only the photoadhesive layer of the exposed area adheres to the silicone rubber layer and remains. In such case, the developing operation is completed by merely peeling off the protecting film without resort to use of the developing liquid anew.

It is possible to selectively elute the photoadhesive layer of the unexposed area by immersing the plate in developing liquid or spraying the developing liquid thereon after peeling the protecting film.

It is possible to expose or heat the entire surface after development as occasion demands to strengthen the adhesion between the photoadhesive layer and the silicone rubber layer and to thereby further improve the durability in long run printing of the plate.

In the following, the present invention will be explained in further detail by reference to examples. The ethylenically unsaturated monomer (photopolymerizable monomer) and the concentrations of the methacryloyl group and the alcoholic hydroxyl group contained therein used in these examples will be shown in Table 1.

Table 1

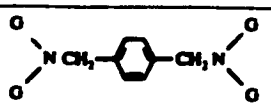
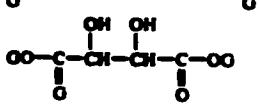
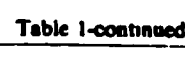
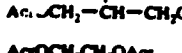
	Photopolymerizable monomer	Chemical structural formula	(Meth)acryloyl group mmol/g	Alcoholic hydroxyl group mmol/g
Example 1	Addition product of 4 mols of GMA/1 mol of xylylenediamine		5.7	5.7
Example 2	Addition product of 2 mols of GMA/1 mol of tartaric acid		4.6	9.2

Table 1-continued

	Photopolymerizable monomer	Chemical structural formula	(Meth)acryloyl group mmol/g	Alcoholic hydroxyl group mmol/g
Example 3	Mixture of glycerin monoacrylate with ethylene glycol diacrylate (weight ratio 24:16)		8.7	9.1
Example 4	Mixture of N-methylolacryl amide with ethylene glycol diacrylate (weight) ratio 24:16)	AcrNHCH OH AcrOCH$_2$CH$_2$OAcr	10.5	5.9
	Pentaerythritol diacrylate	(AcrO)$_2$C(CH$_2$OH)$_2$	9.1	8.1
	Addition product of 1 mol of GMA/1 mol of acrylic acid		9.3	4.6
	Addition product of 1 mol of GMA/1 mol of N-methylol acrylamide		8.2	4.1
Comparative Examples 1 and 2	Ethylene glycol diacrylate	Acr 	11.6	0
	Trimethylolethane triacrylate	CH$_3$C(CH$_2$OAcr)$_3$	10.8	0
	Mixture of ethylene bis-acrylamide with tetraethylene glycol	AcrNH 	8.6	0
	GMA: glycidyl methacrylate			
				
			all based on the entire monomer	

EXAMPLE 1

To an aluminum plate ground by brush, silicone primer "SH 4094 Primer", manufactured by Toray Silicone Co., Ltd. of Japan, was applied to the thickness of 1 μ. Onto the resultant film there was applied a silicone gum solution obtained by diluting RTV Silicone Gum Dispersion, "YE 3085" manufactured by Toshiba Silicone Co., Ltd. of Japan with n-heptane and adding to this diluted silicone gum dispersion benzoin ethylether in an amount of 3% by weight, calculated as solid, and the resultant applied silicone gum solution was dried by air to provide a 5 μ thick silicone gum layer. The silicone gum was a linear diorganopolysiloxane having acetoxy end group at which cross-linking could be produced by the action of atmospheric moisture through emitting acetic acid to give a rubber-like coating. The foregoing assembly will be termed the base and silicone gum layer.

Additionally, a 2 μ thick photoadhesive layer was applied on a 9 μ thick polypropylene film "Torayfan" manufactured by Toray Industries, Inc. of Japan, the photoadhesive layer having the following composition.

(a) Addition product of 4 mols of glycidyl methacrylate with 1 mol of xylylenediamine — 99% by weight

(b) Benzoin methylether — 9% by weight

Next, the base and silicone gum layer and the photoadhesive layer were so pressed together that the surface of the silicone rubber layer was in contact with and adhered closely to the surface of the photoadhesive layer to produce a presensitized planographic printing plate.

On this planographic printing plate, a negative transparency was applied and the two were caused to adhere closely to each other in vacuo. This was then irradiated from a distance of 10 cm for 3 minutes by light from a fluorescent lamp (FL20S-BL360, manufactured by Mitsubishi Electric Co., Ltd. of Japan).

When the "Torayfan" was peeled and the printing plate was then immersed in a 50% aqueous solution of isopropanol and lightly rubbed, the photoadhesive layer of the unexposed area was easily removed, whereas, at the same time the photoadhesive layer of the exposed area was photo-insolubilized and adhered strongly to the underlying silicone rubber layer so that a tenacious image relief remained.

By so doing, a planographic printing plate was obtained which corresponded to the image of the negative transparency throughout the entire printing plate. When this printing plate was mounted on a rotary offset duplicator, "Multilith 1250" manufactured by Addressograph Multigraph Co. and printed out using a printing ink, "Dricolor Black" manufactured by Dainippon Ink and Chemicals, Inc. of Japan, without using water for moistening, excellent printed matter was obtained. The printing press of this example had good image reproducibility and was capable of printing more than 10,000 copies.

EXAMPLE 2

On a crude aluminum plate whose surface had not been treated, a 2 μ thick halation-preventing layer of the following composition was provided.

(a) Styrene — acrylic acid (90:10 weight ratio) copolymer (intrinsic viscosity in cellosolve acetate: 0.3)
95 parts by weight

(b) Michler's ketone — 5 parts by weight

Next, to the surface of said halation-preventing layer, a 1% heptane solution of silicone primer "SH 4094" manufactured by Toray Silicone Co., Ltd. of Japan, was applied and dried.

Additionally, on a 9 μ thick "Torayfan" polypropylene film, a 5 μ thick photoadhesive layer having the following composition was provided.

(a) Copolyamide (a nylon 6 — nylon 66 - 2, 2, 4 -trimethyl hexamethylenediamine adipate (30:35:35 by weight) copolymer — 37% by weight

(b) Addition product of 1 mol of tartaric acid with 2 mols of glycidyl methacrylate 60% by weight

(c) Benzophenone — 3% by weight

(d) Phenothiazine — 0.01% by weight

On this photoadhesive layer, a solution solution obtained by diluting with n-heptane, a heat-curing type silicone gum, "SH 7023" manufactured by Toray Silicone Co., Ltd. of Japan, and adding to the resultant diluted silicone gum dispersion, benzoin ethyl ether in an amount of 3% by weight calculated as solid, was applied and dried by air.

Next, this laminar assembly of "Torayfan," photoadhesive layer and silicone gum was applied under pressure to the aforesaid coated aluminum base plate with the surface of the silicone primer adhering closely to the surface of the silicone gum and thereafter the whole was heated at 100° C for 15 minutes, forming a presensitized planographic printing plate.

On the presensitized planographic printing plate so obtained, a negative transparency was applied and caused to adhere closely to said printing plate in vacuo, and was then irradiated for 2 minutes by light from a high pressure mercury lamp (ORC Jet Light 3000, at a distance of 1 m). The "Torayfan" was peeled off and thereafter the photoadhesive layer of the unexposed area was eluted by washing with modified ethanol. When printing was carried out similarly as in Example 1, good printed matter was obtained.

EXAMPLE 3

On a crude aluminum plate, a halation-preventing layer and a silicone primer layer were provided similarly as in Example 2, comprising a base layer. Additionally, on a 9 μ thick polyethylene terephthalate film, "Lumirror" manufactured by Toray Industries, Inc. of Japan, there was applied a 1 μ thick layer of "Gosenil GH 17", a polyvinyl alcohol manufactured by Nippon Gosei Kagaku Co., Ltd. of Japan, on which a 2 μ thick photoadhesive layer having the following composition was provided.

(a) Ethyl acrylate — methyl methacrylate — acrylic acid (70:20:10 weight ratio) copolymer (intrinsic viscosity in cellosolve acetate 0.4) — 55% by weight
(b) Glycerol monoacrylate — 24% by weight
Ethylene glycol dia- — 16% by weight crylave
(c) Michler's ketone — 5% by weight

To the surface of the photoadhesive layer was applied a solution obtained by diluting a silicone gum, "SH 9/32," manufactured by Toray Silicone Co., Ltd. of Japan, with Naphtha No. 3 (manufactured by Esso) and this solution was then dried by air.

Next, the base layer and the foregoing composite photoadhesive and silicone gum layer were so pressed together that they adhered closely at the interface between the surface of the silicone primer and the surface of the silicone gum, and the assembly thereafter allowed to stand undisturbed for 24 hours.

The photosensitive planographic printing plate so obtained was at first denuded of the covering film to expose the polyvinyl alcohol layer on the surface of the printing plate and a negative transparency was placed on the surface of the polyvinyl alcohol layer, and exposed to light the same as in Example 2. The printing plate which had been exposed to light was easily developed by an aqueous solution of 0.2 N-sodium hydroxide and a strong ink-receptive image relief was produced on the surface of the silicone rubber

EXAMPLE 4

Example 3 was repeated except that in producing the planographic printing plates the monomer components (b) of the photoadhesive layer were replaced by the following compounds.

(a) N-methylolacrylamide — 24% by weight
Ethylene glycol diacrylate — 16% by weight
(b) Pentaerythritol diacrylate — 40% by weight
(c) Addition product of 1 mol of acrylic acid with 1 mole of glycidyl methacrylate — 40% by weight
(d) Addition product of 1 mol of N methylolacrylamide with 1 mol of glycidyl methacrylate — 40% by weight

When planographic printing plates produced in accordance with this example were exposed to light and developed the same as in Example 3, image relief strongly adhering to the surface of the silicone rubber layer were obtained in each case.

Comparati Example 1

Example 3 was repeated except for replacing the photopolymerizable monomer components (b) of the photoadhesive layer by the following photopolymerizable monomers not containing alcoholic hydroxyl groups.

(a) Ethylene glycol diacrylate — 40% by weight
(b) Trimethylolethane triacrylate — 40% by weight
(c) Methylenebisacrylamide — 20% by weight
Triethylene glycol diacrylate 20% by weight

In each case of this comparative example, a relief of the image portion did not strongly adhere to the surface of the silicone rubber layer, but peeled off during the developing opertion or were peeled off by inking rollers upon printing several hundreds of copies, to give incomplete printed matters.

Comparative Example 2

Example 3 was repeated except for replacing the polymer component (a) of the photoadhesive layer by the following polymers having alcoholic hydroxyl groups and replacing the photopolymerizable monomers of (b) of the photoadhesive layer by the photopolymerizable monomers not containing alcoholic hydroxyl groups used in Comparative Example 1.

(a) 40% saponified product of polyvinyl acetate
(b) Ethyl acrylate — styrene — 2-hydroxyethyl methacrylate — acrylamide — acrylic acid (64:14:12:2:8 weight ratio) copolymer (intrinsic viscosity in cellosolve acetate 0.3)
(c) Poly-2-hydroxypropyl methacrylate (intrinsic viscosity in cellosolve 0.2).

As a result of using any one of the above polymers of this comparative example, the adhesion between the image relief and the surface of the silicone rubber layer was very inferior similarly as in Comparative Example 1.

The following is claimed:

1. A negative acting presensitized dry planographic printing place comprising:

(a) a flexible base layer,
(b) a sparsely cross-linked linear diorganopolysiloxane layer overlying said base layer, and
(c) a photoadhesive layer overlying said diorganopolysiloxane layer, and in direct contact therewith comprising at least one photopolymerizable unsaturated compound having a boiling point above 100° C and a photoinitiator wherein at least one said photopolymerizable compound has at least one hydroxyl group and at least one acryloyl group or one methacryloyl group in the same molecule and the total concentration of the hydroxyl groups

and the total concentration of the acryloyl or methacryloyl groups in the photoadhesive layer are each greater than 0.1 mmol/g

2. The negative-acting presensitized dry planographic printing plate of claim 1, wherein at least one kind of said photopolymerizable unsaturated compound is a member selected from the group consisting of

(a) partial esters of acrylic and/or methacrylic acid with polyhydric alcohols having 2 - 12 carbon atoms,

(b) addition product of glycidyl acrylate and/or methacrylate with hydrogen halides, alcohols, thiols, amines, carboxylic acids, sulfonic acids, phenols and phosphoric acids having 1 - 12 carbon atoms,

(c) addition products of acrylic and/or methacrylic acid with epoxy compounds having 2 - 14 carbon atoms,

(d) esters of N-methylolacrylamide or methacrylamide with oxy-carboxylic acids having 2 - 10 carbon atoms,

(e) addition products of N-methylolacrylamide or methacrylamide with epoxy compounds having 2 - 12 carbon atoms.

3. The negative-acting presensitized dry planographic printing plate of claim 1, wherein at least one kind of the said photopolymerizable compound is a member selected from the group consisting of

(a) partial esters of acrylic and/or methacrylic acid with ethylene glycol, propylene glycol, glycerol, trimethylol methane, trimethylol ethane, trimethylol propane, sorbitol and pentaerythritol,

(b) addition products of glycidyl acrylate or methacrylate with hydrogen chloride, methanol, ethylene glycol, trimethylol methane, pentaerythritol, ethanolamine, trimethanolamine, ethane dithiol, methylamine, ethylenediamine, xylylenediamine, aniline, phenylenediamine, acetic acid, acrylic acid, methacrylic acid, malonic acid, succinic acid, maleic acid, fumaric acid, itaconic acid, malic acid, tartaric acid, citric acid, phenol, thiophenol and hydroquinone,

(c) addition products of acrylic and/or methacrylic acid with diglycidyl esters derived from the group consisting of phthalic acid, tetrahydrophthalic acid, succinic acid, adipic acid, maleic acid, fumaric acid and itaconic acid,

(d) diesters of N-methylolacrylamide or methacrylamide with malic acid, tartaric acid, and citric acid, and

(e) addition products of N-methylolacrylamide or methacrylamide with glycidyl esters of acrylic acid, methacrylic acid, phthalic acid, tetrahydrophthalic acid, maleic acid, fumaric acid and itaconic acid.

4. The negative-acting presensitized dry planographic printing plate of claim 1, wherein a halation preventing layer is interposed between said base layer and said diorganopolysiloxane layer such that less than 20% of the ultraviolet light of the wave length from 300 to 400 mμ is reflected.

5. A negative-acting presensitized dry planographic printing plate comprising:

(a) a flexible base layer,

(b) a sparsely cross-linked linear diorganopolysiloxane layer overlying said base layer,

(c) a photoadhesive layer overlying said diorganopolysiloxane layer, comprising at least one photopolymerizable unsaturated compound having a boiling point above 100° C and a photoinitiator, wherein at least one kind of said photopolymerizable compound has at least one hydroxyl group and at least one acryloyl group or one methacryloyl group in the same molecule and the total concentration of the hydroxyl group and the total concentration of the acryloyl or methacryloyl groups in the photoadhesive layer are each greater than 0.1 mmol/g, and

(d) a polymeric layer overlying said photoadhesive layer, capable of transmitting light of wave length from 300 to 400 mμ and protecting said photoadhesive layer from oxygen.

6. The method of preparing the negative-acting presensitized plate of claim 5 which comprises the steps of applying said photoadhesive layer on said polymeric layer and laminating said layers on said diorganopolysiloxane layer previously applied on said base layer with said photoadhesive layer in contact with said diorganopolysiloxane layer.

7. The method of preparing the negative-acting presensitized plate of claim 5, which comprises the steps of applying said diorganopolysiloxane layer on said photoadhesive layer previously applied on said polymeric layer and laminating said layers on said base layer with said diorganopolysiloxane layer in contact with said base layer.

8. The negative-acting presensitized plate of claim 1, wherein said diorganopolysiloxane layer incorporates a photosensitizer in the range of 0.1 - 10% by weight based upon the total weight of the silicone rubber layer.

9. The negative-acting presensitized film of claim 1, wherein said photoadhesive layer consists essentially of

(a) said photopolymerizable unsaturated compound 5.0 - 99.0 parts by weight,

(b) a photoinitiator 0.1 - 10.0 parts by weight,

(c) a heat polymerization inhibitor 0.001 - 1.0 parts by weight, and

(d) a filler for maintaining dimensional stability of said photoadhesive layer 0.01 - 90.0 parts by weight.

10. The negative-acting presensitized plate of claim 5, having a halation-preventing layer between said base layer and said diorganopolysiloxane.

11. The method of preparing the negative-acting presensitized plate of claim 10 which comprises the steps of applying said halation-preventing layer on said base layer, applying said photoadhesive layer on said polymeric layer, applying said diorganopolysiloxane gum layer on said photoadhesive layer, laminating said layers together under pressure with said halation preventing layer in contact with said diorganopolysiloxane layer.

12. The negative acting dry planographic printing plate of claim 1, wherein the surface of said photoadhesive layer in contact with said diorganopolysiloxane layer has been pre-treated with silicone primer.

13. The negative acting presensitized dry planographic printing plate of claim 5, wherein the surface of said photoadhesive layer in contact with said diorganopolysiloxane layer has been pre-treated with silicone primer.

14. A negative acting presensitized dry planographic printing plate comprising:

(a) a flexible base layer of polyethylene terephthalate,

(b) a halation prevention layer on said base layer and comprising a styrene-acrylic acid copolymer and a photoinitiator,

(c) a sparsely cross-linked linear diorganopolysiloxane layer overlying said styrene-acrylic acid copolymer layer,

(d) a photoadhesive layer overlying said diorganosiloxane layer consisting of a composition comprising

(1) an ethylacrylate-methylmethacrylate-acrylic acid copolymer,

(2) the addition product of 4 mols of glycidyl methacrylate with 1 mol xylylenediamine and ethyleneglycol diacrylate, said addition product containing hydroxyl groups and acryloyl or methacryloyl groups and

(3) a photoinitiator; the total concentration of the hydroxyl group and the total concentration of the acryloyl or methacryloyl groups in the photoadhesive layer each being greater than 0.1 mmol/g., and then,

(e) a layer of diorganopolysiloxane capable of transmitting light having a wavelength from 300 to 400 mμ.

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